

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
30 June 2005 (30.06.2005)

PCT

(10) International Publication Number  
WO 2005/059618 A2

(51) International Patent Classification<sup>7</sup>: G02B 13/00

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(21) International Application Number:  
PCT/EP2004/014290

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(22) International Filing Date:  
15 December 2004 (15.12.2004)

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CI, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(25) Filing Language: English

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,

(26) Publication Language: English

(30) Priority Data:  
60/530,623 19 December 2003 (19.12.2003) US  
60/568,006 4 May 2004 (04.05.2004) US

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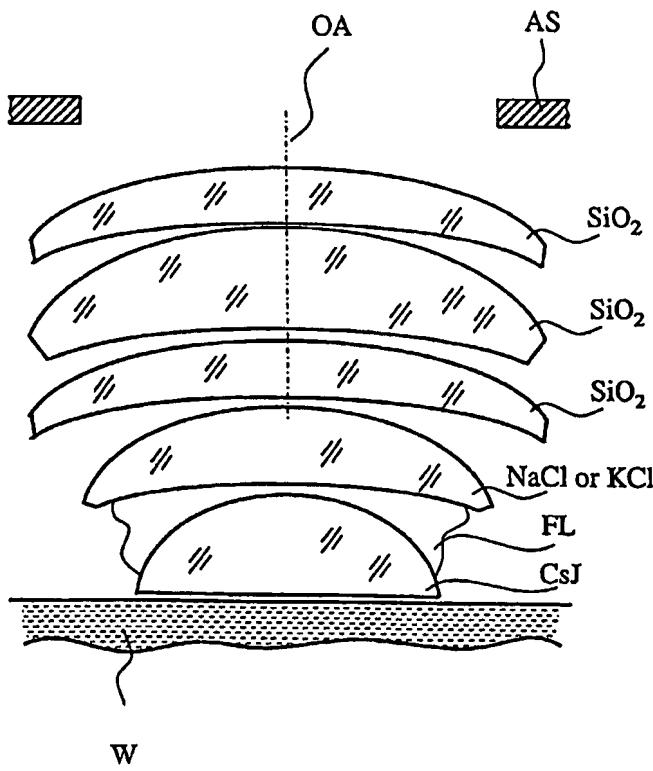
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*[Continued on next page]*

(54) Title: MICROLITHOGRAPHY PROJECTION OBJECTIVE WITH CRYSTAL LENS

WO 2005/059618 A2



(57) Abstract: Very high aperture microlithography projection objectives operating at the wavelengths of 248 nm, 193 nm and also 157 nm, suitable for optical immersion or near-field operation with aperture values that can exceed 1.4 are made feasible with crystalline lenses and crystalline end plates P of NaCl, KCl, KJ, RbJ, CsJ, and MgO, YAG with refractive indices up to and above 2.0. These crystalline lenses and end plates are placed between the system aperture stop AS and the wafer W, preferably as the last lenses on the image side of the objective.



ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17:**

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ,*

*NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)*

- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations of inventorship (Rule 4.17(iv)) for US only*

**Published:**

- *without international search report and to be republished upon receipt of that report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

Microlithography Projection Objective with Crystal Lens

The invention relates to a microlithography projection objective with at least one crystal lens, wherein the  
5 objective is designed in particular for a high numerical aperture and with immersion or optical near field.

From publications such as

10 Bruce W. Smith et al. Optical Microlithography XVII  
Proc. SPIE 5377 (2004), p 273 -284;

Bruce W. Smith et al. Optical Microlithography XVI,  
Proc. SPIE 5040 (2003), p 679 -689;

15 John H. Burnett et al. "High Index Materials for 193 nm  
and 157 nm Immersion lithography"  
Int'l Symp. on Immersion & 157 nm Lithography, Vancouver  
8/2/04 (NIST/ Corning Tropel)

20 and patent applications such as  
WO2004/019 128 A2,

or, commonly owned with this application:  
US 6,717,722 B,  
25 US Ser. No. 10/734,623 filed 15 Dec. 2003,  
US Ser. No. 60/530,623 filed 19 Dec. 2003,  
US Ser. No. 60/530,978 filed 22 Dec. 2003,  
US Ser. No. 60/544,967 filed 13 Feb. 2004,  
US Ser. No. 60/568,006 filed 04 May 2004,  
30 US Ser. No. 60/592,208 filed 29 July 2004,  
US Ser. No. 60/591,775 filed 27 July 2004,  
US Ser. No. 60/612,823 filed 24 Sept 2004,  
DE 10 2004 051 730.4 filed 22 Oct. 2004

some information about this art can be gathered.

Of these, e. g. WO 2004/019 128 A2, US 10/734,623,  
5 US 60/592,208, US 60/591,775 and US 60/612,823 show  
objective designs which can be optimized by and combined  
with the use of materials and teachings according to this  
application.

10 Suitable immersion liquids are inter alia described in US  
60/568,006 or DE 10 2004 051 730.4.

PCT application entitled "Microlithography Projection  
Objective with Crystal Elements", inventor Karl-Heinz  
15 Schuster, filed on December 10, 2004, internal reference  
04213 P PCT, assigned to the same assignee teaches the  
case of certain non-cubic crystals in this context. Each  
can be combined with this invention.

20 All cited documents are incorporated into this application  
by reference in their entirety.

Their citation in no way constitutes any declaration on  
their relevance for this application, and the list  
25 certainly is incomplete and many more publications relate  
to this art.

Crystal lenses consisting in particular of calcium  
fluoride (fluorspar) or other fluorides have been used  
30 until now as a means to achieve a sufficient transmittance  
at wavelengths below 200 nm and down to, e.g., 126 nm, and  
also to achieve a chromatic compensation by using fluoride  
lenses particularly in combination with lens elements of

quartz glass. As a rule, these arrangements involved the use of several crystal lenses in the objective, with diameters exceeding 10 cm and with a combined thickness of the order of 10 cm, where the lenses had to be arranged at 5 different places in the objective, including in particular locations close to the pupil and close to the object. Because of the resulting requirements regarding the homogeneity of the mono-crystals only lenses of calcium fluoride were realized in actual practice.

10

The same material is also known to be suitable for lenses close to a field plane because of its higher radiation resistance associated with a lower degree of compaction compared to quartz glass.

15

To reduce the achievable structure widths in lithography systems, the first approach that always comes to mind is to use shorter wavelengths. However, the shorter the wavelength, the more difficult it becomes to find suitable 20 immersion materials and lens materials with a high refractive index. Attempts have therefore been made to stay with longer wavelengths but find materials that have an even higher refractive index to compensate for the disadvantage of the longer wavelength. For example, in 25 order to obtain the same level of resolution with light of 248 nm as with light of 193 nm, the aperture has to be larger by a factor of 1.285. According to the formula  $NA = k_1\lambda / (\text{structure width})$ , i.e.,  $NA = 0.3 \times 248.338\text{nm} / 50\text{nm}$ , a resolution of 50 nm would require a refractive index of 30 at least 1.49 if a value of 0.3 has been selected for  $k_1$ .

Since quartz glass (fused silica,  $\text{SiO}_2$ ) has a refractive index of 1.506235 at a wavelength of 248 nm, a resolution

of 50 nm for  $k_1 = 0.285$  could be achieved with the available standard material  $\text{SiO}_2$ . However, the next node at 45 nm is not attainable without a change of material.

5 Consequently, it is an object of the invention to propose lens materials with a particularly high refractive index for lenses in the area near the image plane of an objective of the kind described in generic terms in the introductory paragraph, including suitable protector  
10 plates or other elements. If the refractive index is higher than for quartz glass, it is also possible to use materials whose other properties are less ideal, such as calcium fluoride, for individual elements with a thickness of a few millimeters to centimeters.

15 Solutions to the foregoing task are proposed in accordance with the independent claims, with advantageous further developed embodiments being proposed in accordance with the subordinate claims and in accordance with the  
20 description in its entirety.

In accordance with the invention, a material has been found which has a higher refractive index and can meet all other requirements for lithography applications. As a  
25 prerequisite, the material needs to be sufficiently isotropic. However, an intrinsic birefringence in the deep ultraviolet range near the absorption edge has to be tolerated. As a rule, the further away the absorption edge, the smaller are the values of the intrinsic  
30 birefringence. A particularly advantageous selection is achieved if the intrinsic birefringence crosses the zero level at the wavelength being used for the lithography application.

For the 45 nm node and a wavelength of 248.338 nm, sodium chloride (NaCl) was found to be suitable, which at this wavelength has a refractive index of 1.657766. Its 5 intrinsic birefringence is small enough that no compensation is necessary. As it is sufficient to make the last optical element or individual ones among the last elements in the objective from this material, all of the other elements can be of quartz glass, which is preferred. 10 However, one could also use, e.g., calcium fluoride.

The invention will be further explained hereinafter with reference to the drawings, wherein Figures 1 to 8 schematically illustrate sections through the lenses near 15 the image plane of a projection objective according to the invention, including the immersion area and the wafer or another object being exposed to the projection.

The following symbols are used consistently in the 20 drawings:

AS = aperture stop / system aperture  
P = protector plate / protective element  
I = immersion  
25 W = wafer, or the object to be exposed in the image plane  
FL = fluid configured as a fluid lens  
OA = optical axis

30 Figure 1 schematically illustrates the last lenses on the image side of a microlithography projection objective according to the invention with an immersion fluid I, for example 25% D<sub>3</sub>PO<sub>4</sub> in D<sub>2</sub>O (n248 ≈ 1.66), a monocrystalline

last lens of NaCl, with a plane-parallel thin protector plate P or a protective layer placed in between.

For values of  $k_1 = 0.285$ ,  $\lambda = 248.338$  nm and a maximum 5 incidence angle of  $71.8^\circ$  from the normal direction, one finds a minimum refractive index of 1.6556, a condition that is met by sodium chloride with a refractive index of 1.657766. Monocrystalline NaCl is not hygroscopic in air, in contrast to commercially available kitchen salt which 10 contains impurities of MgCl and therefore attracts water. It should be clear that the work operations on NaCl in the production process have to be free of water, because NaCl dissolves in liquid water. However, the appropriate working techniques have been known for decades.

15 Otherwise, the lenses can be coated with vapor-deposited layers and worked on with ion beams. Inside the objective, which is normally flushed with helium or nitrogen, moisture is in any event of no concern.

20 To achieve the 32 nm node at 248 nm requires a large step in the refractive index. One finds that the refractive index needs to come up to slightly more than 2.0. At the same time, it is still necessary to obtain a satisfactory transmittance. According to the invention, the material 25 proposed to meet these requirements is potassium iodide KI with a refractive index of  $n=2.0523$  at 248.338 nm.

Similar to NaCl, potassium iodide is water-soluble but advantageously isotropic. Other representatives of the 30 alkali group in the form of iodides are likewise suitable, including NaI, RbI, CsI.

Since the primary use of iodides is in the infrared range, no raw materials of extreme purity have so far been used to grow crystals for the far ultraviolet range. The transmittance edge for CsI, a material of the highest refractive index, is reported as 227 nm, so that the transmittance values obtained for NaI, KI, RbI tend to be even more favorable.

5 The highest index of refraction is obtained with CsI as it has the highest atomic weight in the alkali group. Already at the present time monocrystalline CsI is grown and commercially distributed for infrared applications. As a special precaution, it needs to be noted that the relative humidity of the ambient air around this crystal 10 may not exceed 35%.

15 Figure 2 shows the end portion of a refractive or catadioptric objective with an aperture of more than 2.0. The wafer W is for example in the optical near field, with a distance of 20 nm. To show an example of a fluid lens 20 FL, a fluid from the group of highly refractive substances that are also known as immersion fluids is arranged between the last two lenses on the image side of the objective.

25 As the iodides of the alkali group are very soft and therefore mechanically delicate, it is recommended to use appropriate protective measures. Proposed is a protector plate of MgO, which has an extremely high refractive 30 index.

For applications at 248 nm and other wavelengths, magnesium oxide MgO has to be produced in crystalline form

with the requisite purity. In the form of a thin element, it is sufficiently transparent. The crystalline oxide material is isotropic and has a coefficient of linear thermal expansion of  $14 \times 10^{-6}/\text{K}$ , while CsI for example has 5 a linear expansion coefficient of  $54.9 \times 10^{-6}/\text{K}$ . In order to safely join these materials by wringing, it is necessary to overlay the iodide with an adhesive layer of a highly refractive material, for example hafnium oxide over CsI.

10

Instead of making the lenses of alkali iodide and protecting them with MgO plates, it is of course also possible to use MgO itself for the one or more last elements if a crystal material of suitable transmittance 15 and homogeneity is used. Given that MgO has very good chemical and mechanical properties and is a most highly refractive material with a refractive index over 2.0, it is suitable for the wavelength of 248 nm, if the crystal quality is appropriately optimized.

20 Instructive comments on this may be found in the paper by John H. Burnett et al. "High Index Materials for 193 nm and 157 nm Immersion Lithography", Intl. Symp. On Immersion + 157 nm Lithography, Vancouver, 2 Aug 2004.

25 Figure 3 represents an example of a refractive or catadioptric projection objective in which the system aperture stop or the conjugate plane of the system aperture stop that is closest to the image plane is followed by a lens group in which the last lens and in 30 this case also the next to last lens on the image side of the objective are lenses of monocrystalline magnesium oxide.

Within the context of the periodic system of elements, MgO has a unique position.

The oxides of the first group, i.e., of the alkali group, 5 are very unstable chemically and therefore not usable. Among the oxides of the second group, the alkaline earth group, ~~the oxide of the lightest element is BeO.~~ While the latter has a good transmittance, it has a wurzite structure and is therefore birefringent. The further 10 oxides MgO, CaO, SrO, BaO have the crystal structure of NaCl and are optically isotropic.

However, the transmittance of CaO, SrO, BaO at 248 nm is inadequate. The lightest element of the third group, 15 boron, forms the compound B<sub>2</sub>O<sub>3</sub>, which is strongly hygroscopic and, by absorbing water, disintegrates into boric acid. The next heavier element, aluminum, forms sapphire crystals which are strongly birefringent. Gallium trioxide (Ga<sub>2</sub>O<sub>3</sub>) in both of its modifications 20 (corundum type / monoclinic) is birefringent. Indium trioxide In<sub>2</sub>O<sub>3</sub> lacks transmittance already for 248 nm and is likewise birefringent.

Magnesium oxide has the further advantage of an excellent 25 chemical stability in contact with many immersion fluids I, which necessarily should likewise have a very high index of refraction at 248 nm. With a system that works in the optical near field, it is important to pay attention to the need for frequent cleaning. Using MgO in 30 the last optical element of the system is advantageous also because of its exceptional hardness and ease of cleaning.

With no immediate need to push up the refractive index at the 45 nm node, it also makes sense to protect an NaCl lens with a thin MgO plate.

5 It is clear that objectives with aperture values of this magnitude have to be designed with extreme asphericities. It is proposed that the high-refractive elements presented above be likewise designed with aspheric surface curvatures.

10 In order to prevent the MgO element from heating up, it is important that the MgO crystal be produced from base material components of the highest purity. A certain amount of absorption can be tolerated as long as MgO 15 serves only as a protector plate that is overlaid on another optical material, because with a small thickness of for example 1.0 mm, the absorption volume, and consequently the heat generation, will remain small. If entire lenses are made of MgO, one should aim for a 20 crystal of high purity.

The 193 nm wavelength, while not yet representing the majority of applications, is an established working wavelength and therefore, as a natural consequence, 25 attractive for a further reduction of the structure widths through the use of very large NA values.

The highest refractive indices presently used in the end-positioned elements which consist of CaF<sub>2</sub> or SiO<sub>2</sub>, are: 30 n = 1.501436 for CaF<sub>2</sub>, at 193.304 nm  
n = 1.560289 for SiO<sub>2</sub>, at 193.304 nm

Chromatic compensation materials with a higher refractive index and a higher dispersion than CaF<sub>2</sub> are known, e.g., from U.S. Patent 6,683,729 B1 (inventor Schuster) and from the aforementioned paper by Burnett et al., including 5 among others the following:

SrF<sub>2</sub>, for 193.304 nm      n = 1.510219

BaF<sub>2</sub>, for 193.304 nm      n = 1.567043

Thus, an objective with a large refractive lens element of 10 BaF<sub>2</sub>, in the end position stands up better to radiation than amorphous SiO<sub>2</sub>, but the refractive index is not significantly increased in comparison to SiO<sub>2</sub>.

In order to safely reach the 32 nm node with the 193 nm 15 wavelength, one needs a sufficiently high refractive index of the last lens element. For example with k<sub>1</sub> = 0.265 a refractive index of 1.658 is needed, or with k<sub>1</sub> = 0.285 a refractive index of 1.812. The photoresists for 193 already reach values as high as n = 1.75 in the best case.

20 A material has now been found which at 193 nm is sufficiently homogeneous and isotropic in the sense of the cubic crystal structure: Potassium chloride KCl has a very good transmittance at 193 nm and more than satisfies 25 the requirement of a refractive index of 1.685. In fact, the refractive index of KCl is 1.756255 at 193 nm. Given that the resists already reach indices up to 1.75, there is a possible application for a system where the light passes from the last lens to the resist on a wafer by 30 means of the optical near field without immersion.

Figure 4 schematically illustrates the part of a projection objective that extends from the aperture stop

plane AS (system aperture plane or a conjugate plane of the system aperture plane) closest to the image field, equipped with KCl lenses according to the invention in near-field distance from a resist / wafer W.

5

Many applications, also at the 32 nm node, can be realized and manufactured more easily with  $k_1$  factors not quite as small as mentioned above. A second optical material has been found which meets the requirements of isotropy and 10 transmittance at 193 nm. In addition, the refractive index is even higher.

Sodium chloride NaCl has a refractive index of 1.829085 at a wavelength of 193 nm. As a result, the  $k_1$ -factor for 15 193 nm and for the 22 nm node can be raised again to 0.287, if one sets a maximum geometric incidence angle of 71.8°. However, with NaCl the absorption edge is slightly closer to 193 nm. Consequently, the contributions to the 20 intrinsic birefringence are larger with NaCl than with KCl.

Therefore, special attention has to be paid to the compensation of the intrinsic birefringence. To compensate the intrinsic birefringence in the case of 25 NaCl, it is proposed to join curved surfaces of NaCl lenses of different crystallographic orientation by wringing (see Figure 4).

It is likewise proposed to perform a compensation by using 30 two different materials. Among other possibilities, this also includes combinations such as NaCl/MgO and NaCl/CaF<sub>2</sub>.

Figure 5 shows an end group of a projection objective configured in this manner with a lens member made of two wrung-together KCl lens elements and as the closing member on the image side two wrung-together monocrystalline NaCl 5 lens elements. The crystallographic orientations of the lens elements are in each case rotated relative to each other for the compensation of birefringence.

Another example is illustrated in Figure 6, where an 10 individual KCl crystal lens is arranged in combination with an NaCl lens member of two wrung-together elements.

The coefficient of expansion is  $36.6 \cdot 10^{-6} \text{ K}^{-1}$  for KCl, and  $39.8 \cdot 10^{-6} \text{ K}^{-1}$  for NaCl. It therefore makes sense and is 15 feasible to join the two different materials by wringing. This is shown schematically in Figure 7.

Because of its large index of refraction, NaCl should be used as the last optical element of positive refractive 20 power. However, since larger amounts of intrinsic birefringence are present in this case, the KCl lens combines a greater refractive power with smaller intrinsic birefringence and favorable transmittance, so that the 25 intrinsic birefringence can be compensated better and the heating of the last double lens can be kept smaller due to the reduced overall amount of absorption.

Consequently, the invention is also directed to the use of the proposed materials in 248 nm or 193 nm lithography 30 applications; to the use of the optical near field or immersion simultaneously with the proposed materials; to the compensation of the intrinsic birefringence in NaCl at 193 nm; to the compensation of the intrinsic birefringence

associated with KCl lenses; to mixed combinations in which KCl and NaCl lens elements are wrung together; to refractive indices larger than 1.75 or larger than 1.82 in lenses; to the use of chlorine compounds as a crystal 5 material for the wavelength of 193 nm; to the location where the materials are used within the objective, i.e., after the aperture stop or after a conjugate location of the aperture stop and before the image plane; to an angle of incidence on the lens surface of at least 60° and 10 preferably larger than 70° in lenses of the proposed materials; and to the use of p-polarized light in these materials.

15 The term "lens" as used herein refers to a refractive optical element of only one material, also often referred to as lens component.

Notwithstanding any of the concepts proposed herein, this 20 optical element can still be coated, in particular with anti-reflex coatings and protective coatings against chemical and physical factors such as being attacked by aggressive chemicals, being dissolved by water or other solvents (moisture protection coating), or against scratching.

25 A further crystal material that has been found suitable for the lens elements of a lithography objective is YAG (yttrium aluminum granate). Its chemical formula is  $Y_3Al_5O_12$ .

30 As a result of the yttrium content in the crystal molecules, the refractive index of YAG is higher than in MgO. In particular for 248 nm, YAG has a good

transmittance. As YAG has been used for many years as a material to grow high-quality crystals for lasers, and with the need to continuously improve these lasers, YAG has in the meantime been developed much farther than for 5 example MgO or spinel  $MgAl_2O_4$ .

~~Besides spinel with an absorption edge at 160 nm and MgO with an absorption edge at 165 nm, YAG is another material that is still sufficiently transmissive at 193 nm.~~

10

Based on the higher index of refraction one can estimate that an absorption edge in YAG lies at about 175 nm. This makes YAG suitable as a material for lithographic projection systems for wavelengths of 248 nm and 193 nm.

15 YAG is basically isotropic but exhibits intrinsic birefringence at 248 nm and in particular at 193 nm, as is also known to occur in CaF<sub>2</sub>, and has been described above for chloride crystals. To compensate this birefringence, it is proposed on the one hand to place at least 2 YAG-  
20 lenses close up to the wafer or on the other hand to use a combination of YAG with MgO, or YAG with spinel, or all of the three kinds of crystals.

Figure 8 illustrates the foregoing concept schematically 25 in an example.

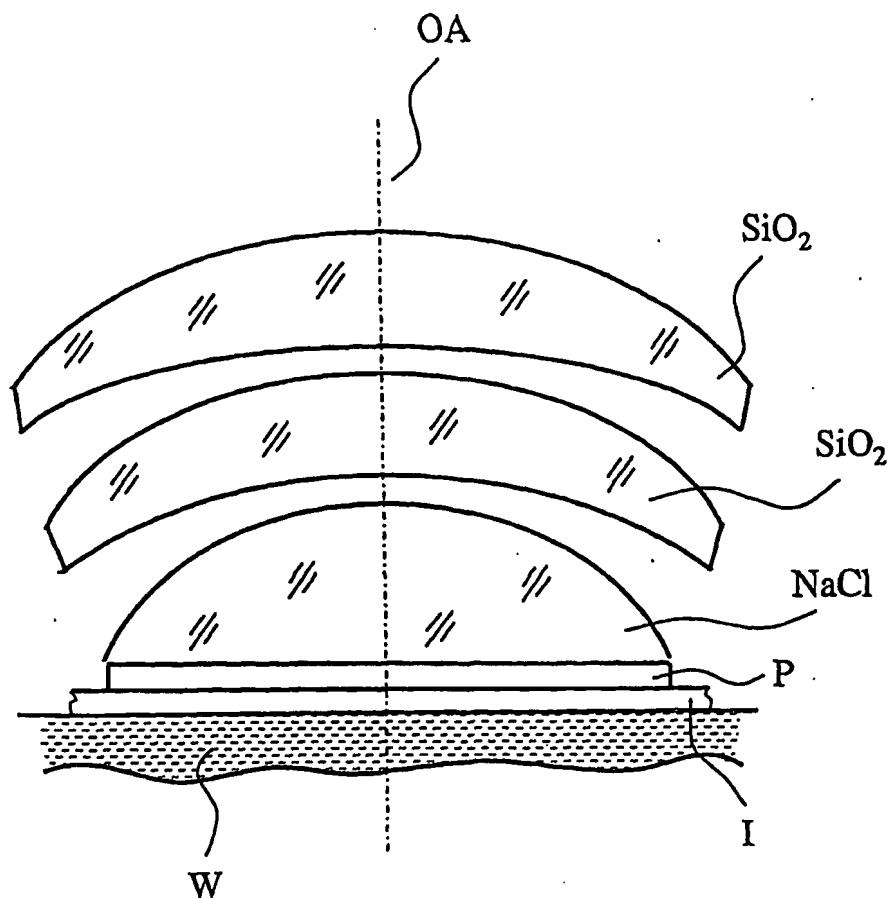
Patent Claims

1. Microlithography projection objective with a numerical aperture on the image side equal to or larger than 1.0, containing at least one lens of a crystal material from the group that comprises NaCl, KCl, KJ, NaJ, RbJ, CsJ, MgO, ~~MgAl<sub>2</sub>O<sub>4</sub>~~, and ~~V<sub>2</sub>Al<sub>5</sub>O<sub>7</sub>~~.
2. Microlithography projection objective according to claim 1, characterized in that the last curved lens on the image side consists of one of the crystal materials named.
3. Microlithography projection objective according to claim 1 or claim 2, characterized in that the numerical aperture on the image side is more than 1.40, preferably more than 1.65, and with special preference more than 2.0.
4. Microlithography projection objective according to at least one of the preceding claims, characterized in that at least one lens of one of the named crystal materials has a moisture protection coating.
5. Microlithography projection objective according to at least one of the preceding claims, characterized in that a plurality of lenses consist of one of the crystal materials named, preferably of different ones, and that the index of refraction at an operating wavelength is highest for the lens that is arranged nearest to an image plane of the projection objective.

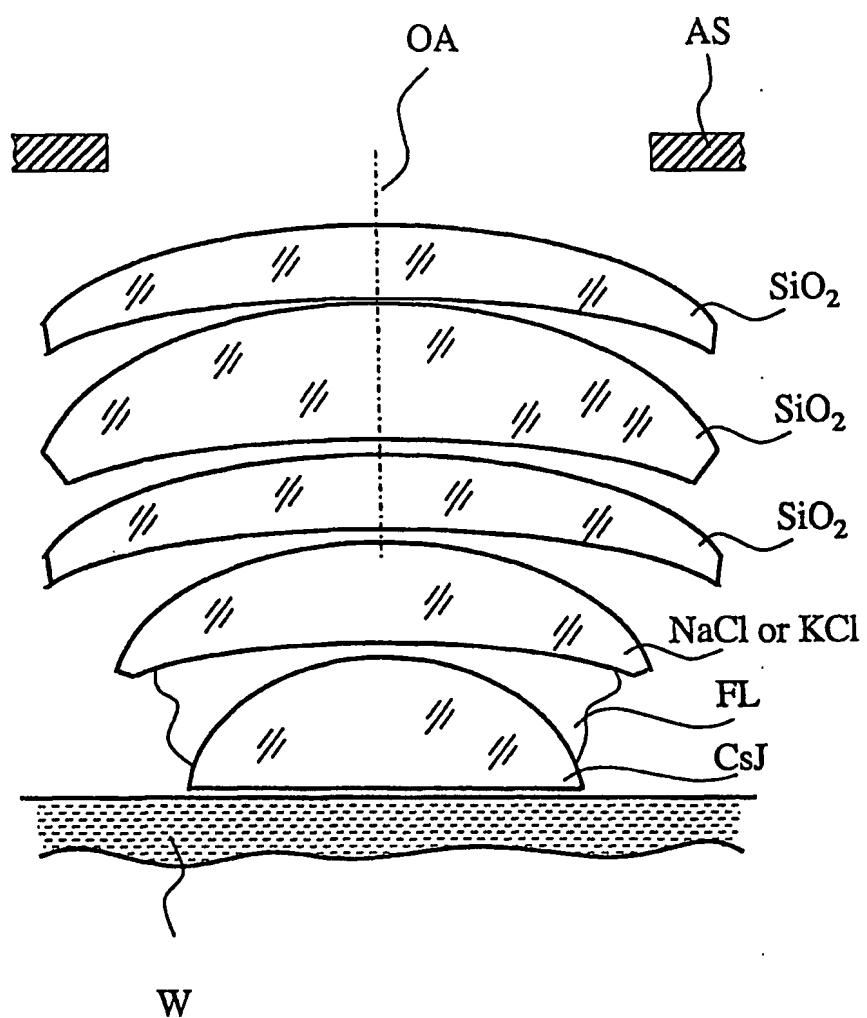
6. Microlithography projection objective according to at least one of the preceding claims, characterized by being configured as an immersion objective.
- 5 7. Microlithography projection objective according to at least one of the preceding claims, characterized by being configured as an optical near field objective.
- 10 8. Microlithography projection objective according to at least one of the preceding claims, characterized by having an operating wavelength from the group comprising 248 nm, 193 nm and 157 nm.
- 15 9. Microlithography projection objective according to at least one of the preceding claims, characterized in that at least one of the lenses of one of the crystal materials named is composed of at least two lens components that are oriented with different crystallographic orientations.
- 20 10. Microlithography projection objective according to at least one of the preceding claims, characterized in that at least one lens is composed of a plurality of components and that at least one of said components consists of a crystal material according to claim 1.
- 25 11. End plate of a microlithography projection objective, consisting of crystalline magnesium oxide which can be overlaid with a coating.
- 30 12. Microlithography projection objective with an end plate according to claim 11, in particular with the features of at least one of the claims 1 to 10.

13. Use of lens components made of crystalline material with a refractive index of more than 1.55, preferably more than 1.6, in an objective of a projection system  
5 conforming preferably to one of the preceding claims, characterized in that at least two of said lens  
~~components made of different crystalline materials are~~  
used in said objective.

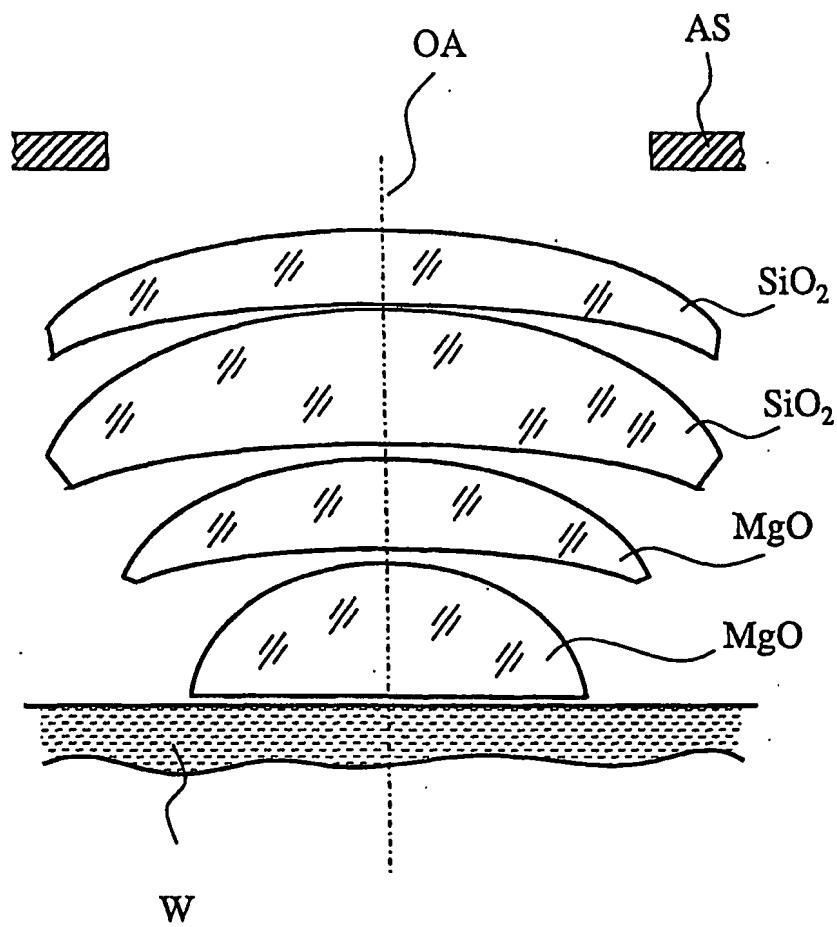
10 14. Microlithography projection system with a microlithography projection objective according to at least one of the claims 1 to 10 and 12, or involving the use of lens components according to claim 13.

**FIG.1**

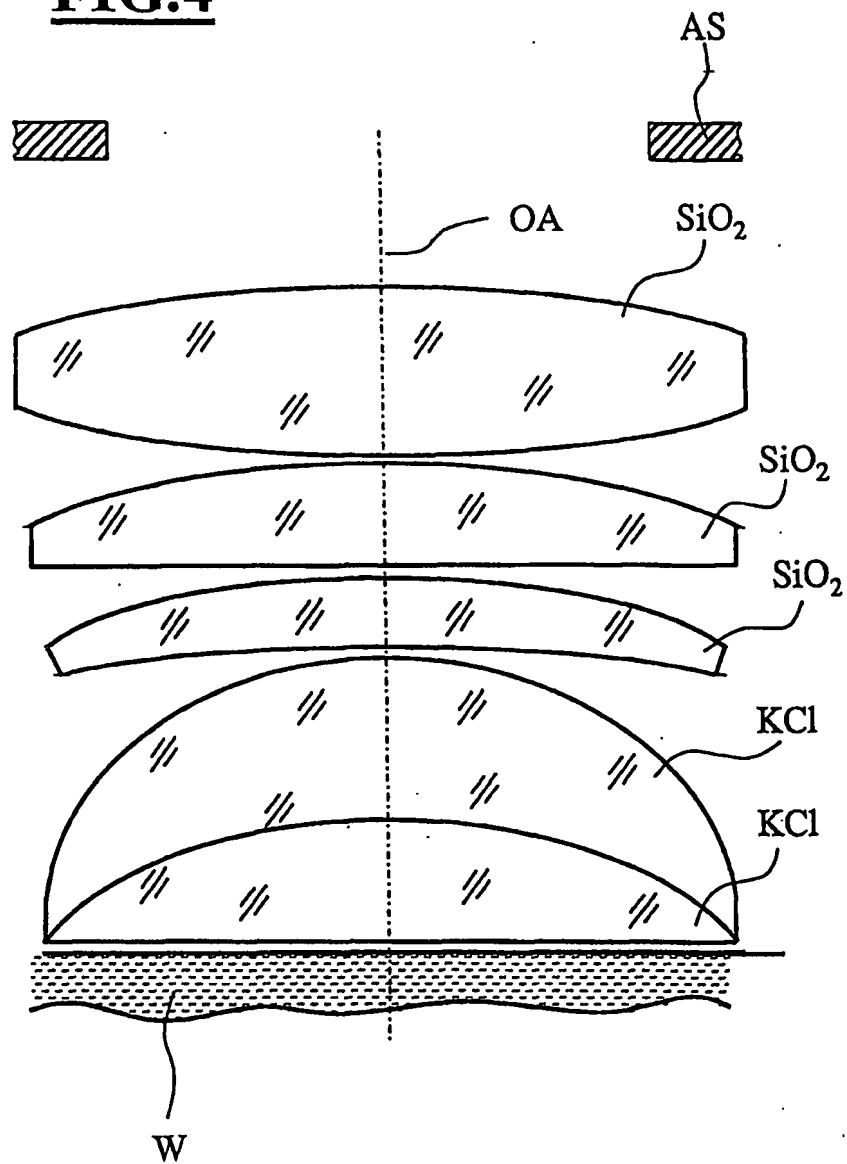
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**FIG.2**

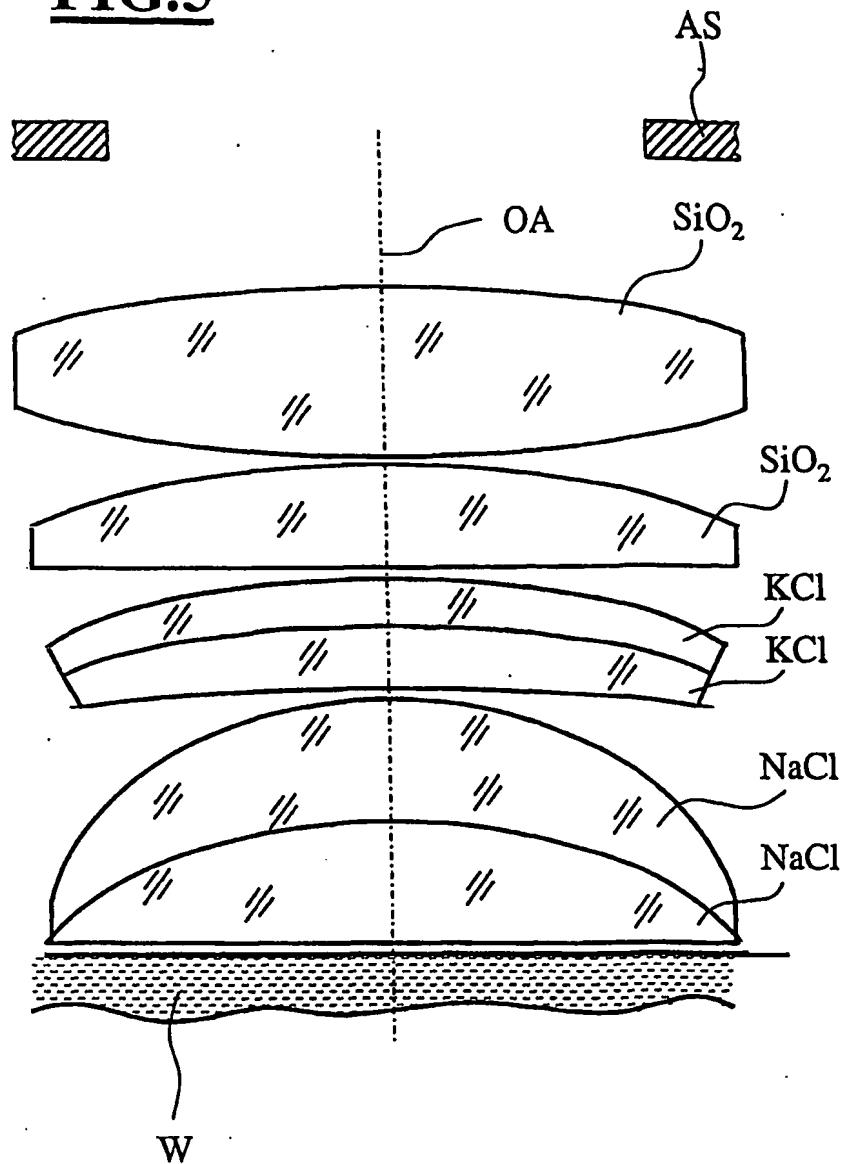
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**FIG.3**

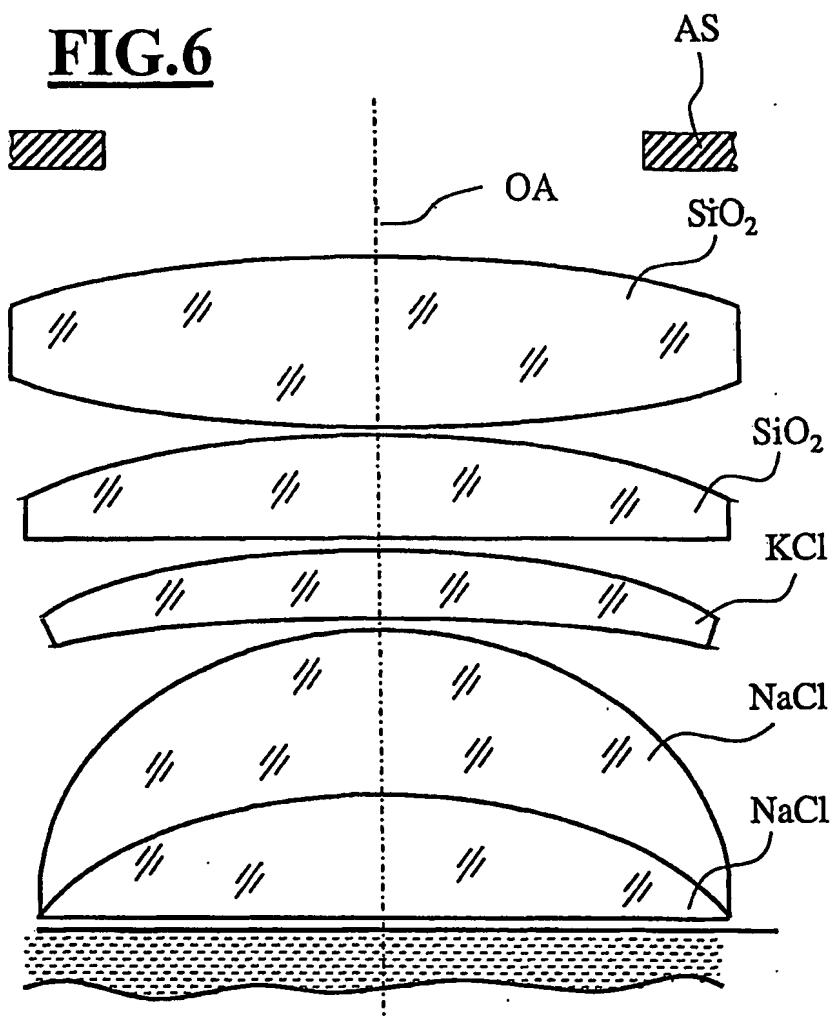
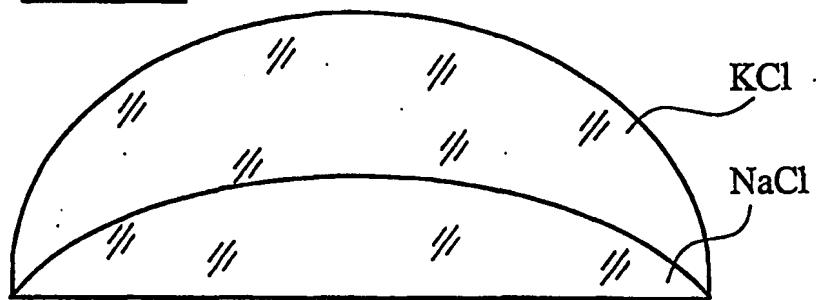
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**FIG.4**

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**FIG.5**

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**FIG.6****FIG.7**

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**FIG.8**